A STUDY OF COMPOUND FORMATION IN SYSTEMS OF TWO SALTS WITH A COMMON ION IN AQUEOUS SOLUTION.

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DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science,
Columbia University.

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BY

WILLIAM F. EHRET, B.S., M.A.

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Dedicated to
MY MOTHER

ACKNOWLEDGMENT

The author wishes to express his thanks and appreciation to Professor James Kendall, at whose suggestion this investigation was undertaken, and whose help and advice have proved invaluable.

The author also wishes to thank Professors Carpenter and Jette for their interest and co-operation during the course of the work.

A STUDY OF COMPOUND FORMATION IN SYSTEMS OF TWO SALTS WITH A COMMON ION IN AQUEOUS SOLUTION.

INTRODUCTION

As early as 1899, Abegg and Bodländer[1] stated that the tendency to formation of complex ions in solution increases as the difference in the electroaffinity of the components increases. In a later paper (1904)[2], Abegg suggested that ionization or dissociation in solution is preceded by compound formation and the latter depends upon the free valences (primary or secondary) of both the solvent and the solute. In the same paper will be found a graphical representation of the elements according to the Periodic Table and in the order of their electroaffinities.

This pioneer work on the relation between compound formation and ionization in solution has been continued, in recent years, by Kendall and his co-workers.[3] Their work has led to the formulation of a general rule, viz., that the degree of stability of an addition compound depends upon the diversity in the positions of the radicals composing the compound in the electrode potential series.[4]

This rule has been found to hold true in systems of the type $HX–H_2O$[4], $ROH–H_2O$[4], HX–RX[5], ROH–RX–H_2O[6], RX–R′X[7], RX–R′X–H_2O[8, 9]. Many hundreds of compounds of the latter type (RX–R′X), with and without water of hydration, have been found to fall in line with the rule that the most stable addition compounds are formed when the positive and negative nature of the components, in this case R and R′, varies most widely. Thus Wells[10] compares nearly five hundred double halides the result being that the above rule is very closely adhered to.

Textbooks and the chemical literature[7, 11, 12] abound with salts of the type RX–R′X with or without water of crystallization. Much fewer and more isolated are records of salts of the

type RX–RX′ with or without water of hydration. Most of the work[6, 13, 14, 15] on systems of this type has been done with mixtures in which RX is a slightly soluble oxide such as in the system forming the compound $CaO \cdot CaCl_2 \cdot 2H_2O$. These may more logically be regarded as systems of the type ROH–RX–H_2O [6] and are in accord with the general rule. Of the remaining cases that have come to hand, of compounds containing the same positive radical with differing negative radicals, several are from the early literature and are based upon qualitative or a single quantitative determination. They are such as BaClF and $BaFNO_3$ [16, 21]; $BaF_2 \cdot BaBr_2$, $SrF_2 \cdot SrBr_2$, $CaF_2 \cdot CaBr_2$ [17]; $BaCl_2 \cdot BaBr_2$ [18]; SrClBr, CaClBr, SrClI [19, 20], all of which were prepared at high temperatures. More recent work has yielded definite proof of the existence of the following compounds of this type: CaClOCl or $CaCl_2 \cdot Ca(OCl)_2$ (chloride of lime) by Lunge and Naef [22]; $CaCl_2 \cdot Ca(C_2H_3O_2)_2$ by Fritzsche and Rammelsberg[23]; $NH_4NO_3 \cdot NH_4HSO_4$ by Wöhler and Schäffer[24]; $(NH_4)_2 0.5SO_4 \cdot 0.5(NO_3)_2$ and $(NH_4)_2 0.4SO_4 \cdot 0.6(NO_3)_2$ by Osaka and Inouye[25]; SnClI, SnBrI, SnClBr by Karantassis[26]; $Na_2SO_4 \cdot NaNO_3 \cdot H_2O$ by Hamid [27]. It has also been definitely shown that no double salts are formed in the system $NaNO_3$–NaCl–H_2O [28] from 0 to 100 degrees Centigrade.

From these few compounds of the type RX–RX′ it will be seen that it is not at all unlikely that there can exist in contact with solution a great many more compounds of this type than have hitherto been investigated. Furthermore it will be noticed from those above mentioned that some compounds of this type do not seem to fall in with the general rule concerning electrode potential diversity and compound formation. On the contrary they seem to contain components that are very closely alike. These combinations can only be interpreted on the basis of substitution compounds having been formed. The components were evidently so nearly alike that one could substitute for the other. Examples of similar substitutions can be found in such compounds as are formed between Li_2SO_4 and K_2SO_4 and between RbOH and NaOH [7]. This question will be discussed in detail later.

The compounds of the type RX–RX′ listed above also seem to be in accord with a rule very familiar to those working with complex salts[1, 4, 29] i. e., that the tendency toward the formation of complexes, including double salts, complex salts and hydrates, increases as the electrode potential decreases. Thus a cation such as Sn or Ca is much more likely to add neutral groups and become complex than Na, NH_4 or K.

The author has continued the work along these lines and has investigated several systems containing two alkaline earth salts and it is believed that from these, general conclusions can be drawn regarding the behavior in solution of quite a series of mixtures of the type RX–RX′–H_2O in which R is an alkaline earth. The anion pairs chosen were Cl and NO_3, and Cl and ClO_3, all strongly negative in character, the purpose being to see whether complex compounds would be formed in solutions of very soluble, highly ionized alkaline earth salts containing anions both strongly negative in character and not much different in point of electrode potential.

It is hoped that with the aid of such rules as have been mentioned and such studies as will be outlined, it will eventually be possible to make a statement of the general rules governing the system RX–H_2O, i. e., for the process of ionization. Up until the present, in all experimental methods for estimating the degree of dissociation of electrolytes in solution, the correct interpretation of the results is conditioned by correct assumptions as to the nature of the substances present in solution. The presence of complex or intermediate ions frequently render the experimental results exceedingly difficult to interpret. It is only by a further study of the formation of complexes in solution that the final result will be attained.

After the work on the alkaline earth systems was well under way the following system, $Pb(NO_3)_2$–KNO_3–H_2O, was brought to the attention of the author. Glasstone and Saunders[30], working on this system, determined the isotherms at 25, 50 and 100 degrees Centigrade. Their reason for investigating the system was their belief in the existence of a complex compound of $Pb(NO_3)_2$ and KNO_3 in water solution. Several previous investigations had shown that the solubility of

$Pb(NO_3)_2$ in water was markedly increased [31] by the addition of KNO_3. The increase was attributed to the formation of double molecules in solution and cryoscopic measurements by Leblanc and Noyes[31] seemed to support this view. They found that mixtures of KNO_3 and $Pb(NO_3)_2$ did not depress the freezing point of water as low as would be expected taking into consideration the common ion effect. Lewis[32], from electromotive force measurements, concluded that complexes must be formed upon adding the aforementioned salts to water for he found a diminution of plumbous ion concentration whenever KNO_3 was added to a solution of $Pb(NO_3)_2$. These conclusions are substantiated by the measurements made by previous investigators[33, 34, 35]. Furthermore, Burrage[36], while investigating the closely related systems $KCl–PbCl_2–H_2O$, $KBr–PbBr_2–H_2O$ and $KI–PbI_2–H_2O$, found stable double salts, capable of existing in aqueous solution, in each of the three systems.

Although Glasstone and Saunders (loc. cit.) found no stable double salt in the system at 25, 50, and 100 degrees the character of their isothermal solubility curves (see dotted curves Fig. IV) showed distinctly that the solubility influence exerted by KNO_3upon $Pb(NO_3)_2$ was the more decided the lower the temperature i. e., the complex, if such exists, is more stable at lower temperatures.

All these considerations, together with some preliminary experiments which seemed to show that at 0 degrees a solid phase different from pure KNO_3 or pure $Pb(NO_3)_2$ separated from a saturated solution containing the two salts, led the author to believe that a solubility determination at 0 degrees over the whole range of concentrations would establish the existence of an addition compound of the two salts. The system was therefor investigated and the results are given in the following.

PREPARATION OF MATERIALS.

$CaCl_2 \cdot 6H_2O$ was at first obtained by three successive recrystallizations from distilled water of Merck's C.P. $CaCl_2 \cdot 6H_2O$. This method resulted in the loss of about one-quarter to one-half of the material due to the extreme solubility and the deliquescent character of the crystals. Later the salt was obtained pure by a more economical method due to Morgan[37] in which the salt is melted in its own water of crystallization and then recrystallized. To insure their neutrality the finished salts were always tested colorimetrically for acidity or alkalinity. Qualitative tests for common impurities were negative.

$CaCl_2$·anhydrous was prepared from the pure hexahydrate by heating in a Freas electrically heated air oven to 110 degrees for several days. A test run, covering a period of nine hours, showed that during this interval no hydrolysis of the $CaCl_2$ had occurred whatsoever. This is in accord with the observations of Dibbits[38] who found that if $CaCl_2 \cdot 6H_2O$ is dehydrated at 130 degrees Centigrade no hydrolysis occurs. The salt was kept in a vacuum desiccator.

$Ca(NO_3)_2 \cdot 4H_2O$ was prepared by triple recrystallization of the Baker and Adamson C.P. crystals. Later an improved method similar to that outlined under $CaCl_2 \cdot 6H_2O$, was used.

$Ca(NO_3)_2$·anhydrous was made by heating the purified crystalline salt in an air oven as under $CaCl_2$ anhydrous. During the process of dehydration tufts of anhydrous $Ca(NO_3)_2$ grow up out of the liquified salt. These are easily removed and the process amounts to a recrystallization as well as a dehydration. The anhydrous salt was tested as was the $CaCl_2$ anhydrous, and then stored in vacuum desiccators.

$Ca(ClO_3)_2 \cdot 2H_2O$. This salt as purchasable is an imported product and the small quantity kept in stock by a large retailer of chemicals was found to be so impure as to make many crystallizations, with consequent losses, necessary. It was thought best to prepare the salt in large enough quantity in the laboratory and for this purpose a new method of preparation was devised. Previous methods[39, 40, 41, 42], although they fur-

nished valuable ideas for the new method, were either not considered to yield a pure enough product or were considered too dangerous to work with. The method devised is as follows:

850 grams of C.P. Barium Chlorate crystals are dissolved in two liters of distilled water. About a liter of boiling hot solution of $(NH_4)_2SO_4$, containing enough salt to precipitate almost all the Barium, is added with stirring to the $Ba(ClO_3)_2$ solution. The remaining Ba ion is precipitated with a dilute solution of $(NH_4)_2CO_3$. Complete removal of the Barium is tested for with the sulphate test. The precipitated sulphate and carbonate are allowed to settle and the solution of NH_4ClO_3 removed by filtration. To the solution is added, with stirring, a calcined lime paste containing sufficient chemically pure lime to release all the ammonia and a slight excess. The mixture is then boiled until no more ammonia is driven off. After cooling, the mixture is filtered and the slight excess of lime is neutralized by means of $HClO_3$ using phenolphthalein as an indicator. The $HClO_3$ is prepared in very dilute solution by the method of Bernard[43]. The resulting solution containing $Ca(ClO_3)_2$ is boiled down until a drop crystallizes. The crystals obtained by recrystallization contain no impurities except a trace of Cl ion which is not detrimental in the work in hand.

$SrCl_2 \cdot 6HO$ and **$Sr(NO_3)_2 \cdot 4H_2O$** were obtained by recrystallizing the so-called chemically pure crystals of the salts from distilled water.

$Pb(NO_3)_2$ and **KNO_3** were obtained by recrystallizing the C.P. products from distilled water. Qualitative tests showed the absence of all foreign substances in the purified product.

APPARATUS AND CHEMICALS.

The bottles used throughout the experiments to contain the various mixtures of salts and water were of Non-Sol glass. The necks and stoppers of the bottles were paraffined before immersion in a water or ice bath in order to exclude all foreign substances. The systems at 25 degrees were run in a thermostat provided with a Freas regulator, the temperature being kept constant at 25.0 degrees plus or minus 0.01 of a degree. The Beckmann thermometer used was frequently checked against a Bureau of Standards thermometer.

The solutions and salts in the bottles were rotated in the thermostat in a manner already described by Nyland [6]. The method insures complete mixing of the solid and liquid phases, the former being kept always in suspension.

In the system run at 0 degrees the thermostat consisted of a well insulated glass battery jar containing a mixture of pure ice and water. While the two phases of water co-existed the temperature obviously varied very little from 0 degrees Centigrade. Both the bath and the mixtures in the bottles suspended in the bath were kept well stirred by the device which rotated the bottles. This consisted of a clamp which gripped the bottle by the neck and stopper and which was rotated quite rapidly by an ordinary stirring motor.

The balance used for weighing was of the type giving accurate results to 0.0001 gram for weights up to 50 grams.

The Westphal balance used in some of the density measurements was checked against pure water at 25 degrees and found to be accurate to four significant figures in a density reading.

The chemicals used in the methods of analysis were all of C.P. quality. The burette and pipettes used throughout were calibrated at 25 degrees C.

EXPERIMENTAL PROCEDURE.

In all the systems the various mixtures of salts and water were made by starting with a bottle containing only one salt and water and in each subsequent run more of the second salt was added to the solution and solid left from the previous run. In the systems $CaCl_2$–$Ca(NO_3)_2$–H_2O and $CaCl_2$–$Ca(ClO_3)_2$–H_2O it was frequently necessary to add the dehydrated salts, since, as will be seen later from the isotherms, certain mixtures of the hydrated salts will dissolve completely in their own water of hydration without the addition of any water whatsoever. Two days of rotation in the bath was found by experience to be the minimum length of time necessary to bring the solution and the crystalline residues to equilibrium. However, due to other duties, the author usually allowed the bottles to rotate from four days to a week, thus insuring true equilibrium conditions. In establishing the composition of the new double salt in the system $CaCl_2$–$Ca(NO_3)_2$–H_2O the bottles containing the saturated solutions in contact with the double salt were kept in the thermostat for over six months and then re-rotated to insure perfect equilibrium conditions. In all cases in which it was doubtful whether equilibrium had been established, the mixture was rotated for three or four days longer and then reanalyzed. It was found by experiment that exactly the same point of equilibrium was reached whether the solution in contact with the solid was heated up to 25 degrees in the bath or whether a solution saturated at a higher temperature was cooled down to 25 degrees while turning in the bath. The latter method was found quicker, since the dehydrated salts can be brought into solution much more readily. In all cases the bottles were re-opened, after they had reached the temperature of the bath, and inoculated with the crystal variety that was thought to be the one which would exist in stable equilibrium with the solution at that temperature.

After the mixtures had come to equilibrium and while still in the bath, samples of the liquid were withdrawn by means of a pipette provided with a folded filter paper at its lower end. Often, especially when the solutions were viscous, suction ap-

proaching within 2–3 mm. of complete vacuum was necessary to suck up a sufficient amount of the solution. The solution was immediately deposited in a specific gravity bottle, brought to 25 degrees, and weighed. At the same time about 10–15 grams of the crystals from the same bottle were weighed as quickly as possible to prevent any evaporation or absorption of moisture. The weighed samples were then diluted to 500 cc. in a volumetric flask and 10 cc. taken for analysis. In the case of the $Pb(NO_3)_2$–KNO_3–H_2O system the samples were not diluted, but dried directly. The $Pb(NO_3)_2$ and KNO_3 present were determined by a method used by Glasstone and Saunders[30], whereby the lead is precipitated and weighed as $PbSO_4$ according to Treadwell and Hall [44]. The water present is determined by drying the samples withdrawn, first at 65 degrees overnight, and then at 130 degrees for 3–4 hours to constant weight. The potassium is determined by difference. The method was tested on known mixtures of $Pb(NO_3)_2$, KNO_3 and water and was found to deviate not more than one part in three hundred on the average.

The method of analysis used in the $SrCl_2$–$Sr(NO_3)_2$–H_2O system was as follows: Strontium was determined as carbonate according to Scott [45], the same method having previously been used by Harkins and Paine[46] in a partial analysis of the same system. Chlorine was determined volumetrically by Mohr's method as described by Scott [47]. The nitrate was determined by difference.

The method used in the $CaCl_2$–$Ca(NO_3)_2$–H_2O and $CaCl_2$–$Ca(ClO_3)_2$–H_2O systems was as follows: Calcium was first precipitated as the oxalate and then determined volumetrically with $KMnO_4$ according to the methods of Scott [48] and of Griffin[49]. Chlorine was determined volumetrically by the method of Mohr[47]. The nitrate or chlorate radical was determined by difference. In both analyses blanks were avoided by standardizing the $KMnO_4$ directly against known weights of pure $CaCO_3$ and the $AgNO_3$ directly against known weights of pure NaCl (Sörensen), the regular procedure of analysis being used in the standardization. The chloride determinations were found to check satisfactorily with determinations made gravi-

metrically and the values obtained for calcium when the $KMnO_4$ was standardized directly against $CaCO_3$ were in agreement with the values obtained when the reagent was standardized against pure sodium oxalate.

In all cases the weights of the two salts present per 100 grams of water and the weight percentages of salts and water per 100 grams of solution were calculated. Molecular percentages were not calculated because the plotting of them would obscure the results in that the curves would all be crowded into the H_2O apex of the ternary diagram.

EXPERIMENTAL RESULTS.

Method of Plotting:

The results are plotted according to a method first used by Gibbs [50] and later by Roozeboom[51, 52], Schreinemakers[53] and many others[54, 55, 56, 57, 58, 59, 60, 61] working in this field. The method of "indirect" analysis or the "rest" method of obtaining the composition of the solid phase in equilibrium with a solution has been employed. The systems studied are condensed ternary systems in which both the pressure and temperature have been fixed ($t = 25.0$ degrees; $p = 760$ mm. assumed). In such systems according to Gibbs the sum of the number of phases and the number of degrees of freedom is equal to the number of components, in this case three. Thus when three phases are present the system has no degrees of freedom and is at an invarient equilibrium point; the composition of the liquid phase will remain constant regardless of the amounts of solid present. Should only one solid phase be in equilibrium with a solution then the system possesses one degree of freedom and the concentration of the salts in the saturated solution may vary over a considerable range.

When expressing the concentration of each component as a weight percentage of the whole, a graphical representation of the system in equilibrium is obtained by means of an equilateral triangle the length of whose side represents 100% and its vertices the pure components S_1, S_2, and water. In order to obtain the percentage amount of a component in a phase represented by a point P within the equilateral triangle, it is only necessary to measure the distance of P from the side opposite that component in a direction parallel to one of the other sides.

In order to establish the composition of the solid phase which is in equilibrium with solutions along a portion of the solubility curve, analyses of both the solutions and the wet crystals that were in equilibrium with the solutions is necessary. Lines drawn through the points representing the solutions and their respective crystal "mushes" will intersect in a common point which establishes the composition of the solid

phase in equilibrium with the solutions examined. Should the solid phase be one of the original salts the lines will intersect at a point on the edges or sides of the equilateral triangle.

In all the systems, except the last, the density of each liquid phase is recorded so that the results can be expressed in terms of normality should this prove necessary at some subsequent time.

The System $CaCl_2$–$Ca(NO_3)_2$–H_2O at 25 degrees C. Figure I and Table I.

According to Roozeboom[62] the solubility of $CaCl_2$ at 25 degrees C. is 82.0 grams per 100 grams of water, or 44.77 weight per cent. Later and more exact experiments by Roozeboom[63] show the solubility to be 81.67 grams per 100 grams of water at 25.05 degrees C.

The solubility of $Ca(NO_3)_2$ is given by Bassett and Taylor[64] as 57.98 grams per 100 grams of solution, and by Cameron and Robinson[65] as 139.30 grams per 100 grams of water. The author's experimental results are in excellent agreement with these previous determinations.

It will be seen from Figure I that the solid phase in equilibrium with saturated solutions along the first branch of the curve, beginning at the left, is $CaCl_2 \cdot 6H_2O$. Along the next branch of the solubility curve, the crystals in equilibrium with the saturated solution are $CaCl_2 \cdot 4H_2O$. Ordinarily the tetrahydrate cannot exist in contact with aqueous solutions at a temperature as low as 25 degrees C.[62] It is only when a substance which itself has a strong affinity for water (in this case $Ca(NO_3)_2$) is present that the formation of the hexahydrate is prevented and the tetrahydrate can exist in contact with aqueous solutions at 25 degrees. Further illustrations of this phenomenon will be found in the next two systems as well as in many others in the literature. A typical case is the dehydration of $CuSO_4 \cdot 5H_2O$ when H_2SO_4 is added to a saturated solution of the salt[66].

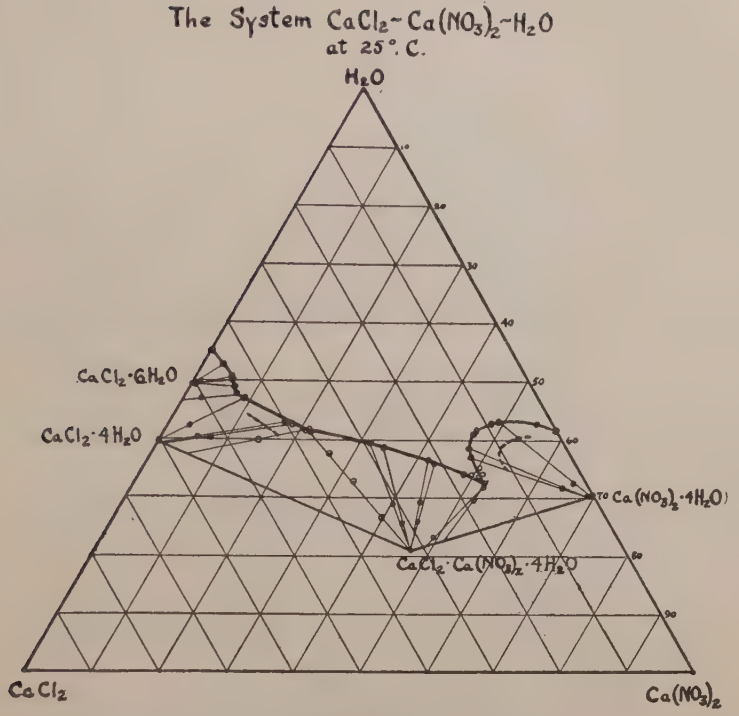

FIGURE I

The crystals above mentioned are the alpha modification of the tetrahydrate according to Roozeboom[62]. At 20.55% $Ca(NO_3)_2$, a reaction takes place:

$$CaCl_2 \cdot 4H_2O + Ca(NO_3)_2 \cdot 4H_2O = \text{Double Salt} + 4H_2O$$

This is a ternary invarient point and three phases, namely, double salt, $CaCl_2 \cdot 4H_2O$, and saturated solution, can exist together. Another ternary invarient point is found at the other end of the solubility curve of the double salt, here the aforementioned reaction also occurs.

The right hand branch of the solubility curve passes through solutions saturated with $Ca(NO_3)_2 \cdot 4H_2O$.

An interesting thing about this system is that very often when crystals of the hexahydrate of $CaCl_2$ and the tetrahy-

TABLE I.

The System $CaCl_2 - Ca(NO_3)_2 - H_2O$
at 25 degrees C.

SOLUTION					REST				
$CaCl_2$		$Ca(NO_3)_2$			$CaCl_2$		$Ca(NO_3)_2$		
gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	Density 25 deg.	gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	Solid Phase
0.00	0.00	140.2	58.35	1.579					$Ca(NO_3)_2 \cdot 4H_2O$
5.29	2.26	129.1	55.08	1.581					
18.08	7.78	112.9	48.88	1.588	6.36	2.06	202.9	65.59	"
19.24	8.24	114.3	48.93	1.590					
21.81	9.19	115.7	48.72	1.595					
28.75	12.02	110.5	46.17	1.616					
31.80	12.91	114.4	46.45	1.625					
37.88	14.57	122.0	46.94	1.655	4.07	1.20	233.7	69.21	"
40.83	15.06	130.2	48.01	1.696	13.48	4.22	205.7	64.46	"
41.91	14.73	142.6	50.11						
42.19	14.45	149.7	51.30	1.713					
47.14	15.75	152.2	50.86	1.790					
46.63	15.20	160.2	52.21	1.749	61.63	18.33	174.6	51.91	$Ca(NO_3)_2 \cdot 4H_2O$+
50.47	16.00	165.0	52.29	1.755	120.5	27.80	213.0	49.12	D.S.

50.05	16.92	145.7	49.28	1.733	86.01	23.57	178.8	49.02	$Ca(NO_3)_2$·
49.80	17.17	140.3	48.37						$CaCl_2 \cdot 4H_2O$
58.80	21.10	119.9	43.02	1.700	92.06	26.74	152.1	44.18	"
59.85	21.75	115.4	41.92	1.692	112.3	28.82	177.4	45.54	"
72.15	27.57	89.60	34.20	1.660	125.5	31.68	170.7	43.07	"
73.63	29.01	80.30	31.63	1.651	106.8	30.71	141.0	40.54	"
91.32	37.04	54.88	22.29	1.623	129.7	33.95	152.4	39.88	"
88.82	36.80	52.61	21.80	1.624					
87.82	36.87	50.38	21.15	1.630	105.8	34.57	100.3	32.77	"
89.60	37.36	50.22	20.94	1.630	95.95	36.16	69.41	26.17	"
90.38	37.73	49.23	20.55	1.630	119.6	46.47	37.80	14.69	$CaCl_2 \cdot 4H_2O$+D.S.
94.22	39.75	42.83	18.07	1.630	133.1	52.75	19.27	7.64	$CaCl_2 \cdot 4H_2O$
94.30	40.35	39.41	16.86	1.619	137.1	54.67	13.75	5.48	"
92.76	43.78	19.14	9.03	1.556	128.6	54.56	7.10	3.01	"
94.82	44.98	16.03	7.60	1.541	107.6	50.47	5.58	2.62	$CaCl_2 \cdot 6H_2O$+ $CaCl_2 \cdot 4H_2O$
90.20	44.24	13.73	6.74	1.523	102.1	50.06	1.93	0.95	$CaCl_2 \cdot 6H_2O$
88.30	44.19	11.54	5.77	1.524	102.7	50.57	0.00	0.00	"
87.54	44.14	10.78	5.43	1.524	100.7	50.17	0.00	0.00	"
85.51	44.75	5.64	2.95	1.474	99.05	48.99	3.12	1.54	"
81.52	44.92	0.00	0.00	1.453					"

drate of $Ca(NO_3)_2$ are brought together a completely liquid mixture results. That this must be so can be seen from Figure I. A line joining the points marked $CaCl_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ represents all possible mixtures of the solid salts[52], and we see that this line would cut the ternary solubility curve in two places and for a considerable space run through the field of unsaturated solutions. Mixtures of the two salts along this part of the line will liquify with the formation of unsaturated solutions.

Below the portions of the ternary solubility curve in equilibrium with $CaCl_2 \cdot 4H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ will be found the incomplete solubility curves (broken line) in this system at 30 degrees as found by Barbaudy[67]. Because of the extreme viscosity of the saturated solutions formed he obtained no further data. However, the slope of the curves agrees with the slope at 25 degrees and it is therefor very likely that the double salt exists at 30 degrees and possibly over even a greater range of concentrations.

According to Figure I a solution containing the two salts in approximately the ratio of 60 grams $Ca(NO_3)_2$ to 40 grams $CaCl_2$ should upon isothermal evaporation at 25 degrees C. yield only crystals of the double salt. Furthermore, the double salt if brought into contact with water at 25 degrees C. will not be decomposed but will continue to dissolve until a saturated solution is formed.

The percentage composition of the double salt was found by carefully plotting the results on a large scale.

The System $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25 degrees C. Figure II and Table II.

The only information available thus far about the solubility of $Ca(ClO_3)_2$ is that by Mylius and Funk [68] at 18 degrees C. They found the solubility to be 177.8 grams per 100 grams of water, or 64%.

The solubility curve of this system has three branches and shows the absence of any double salt at this temperature. The

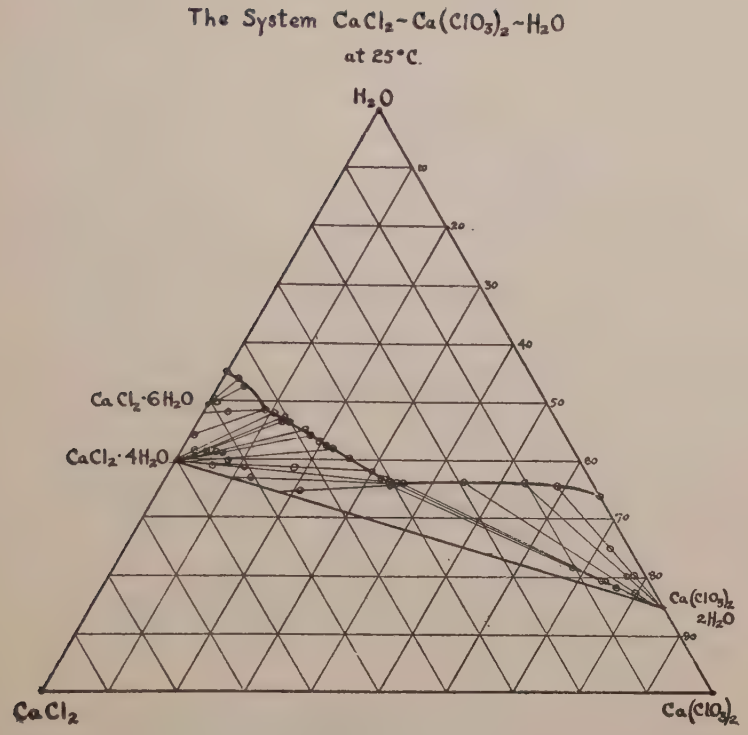

FIGURE II

first branch is in equilibrium with $CaCl_2 \cdot 6H_2O$, then a reaction occurs:

$$CaCl_2 \cdot 6H_2O = CaCl_2 \cdot 4H_2O + 2H_2O$$

and the solution becomes invarient while the two hydrates are present.

The middle branch of the solubility curve represents solutions in equilibrium with the tetrahydrate of $CaCl_2$. To the right we reach a second invarient point after which, upon addition of further amounts of $Ca(ClO_3)_2$, we pass along the third branch of the curve. Along this branch $Ca(ClO_3)_2 \cdot 2H_2O$ is in equilibrium with the saturated solutions.

From this curve and that in Figure I it can readily be seen why $CaCl_2 \cdot 4H_2O$ cannot exist alone in the presence of water at

TABLE II.

The System $CaCl_2 - Ca(ClO)_3)_2 - H_2O$
at 25 degrees C.

SOLUTION					REST				
$CaCl_2$		$Ca(ClO_3)_2$			$CaCl_2$		$Ca(ClO_3)_2$		
gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	Density 25 deg.	gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	Solid Phase
0.00	0.00	194.3	66.05	1.781					$Ca(ClO_3)_2 \cdot 2H_2O$
16.52	5.86	165.1	58.65	1.767	9.74	1.96	386.1	77.89	"
28.42	10.31	147.3	53.45	1.751	15.52	3.08	388.3	77.07	"
52.94	19.19	123.0	44.59	1.731	22.40	3.70	482.8	79.75	"
78.63	28.15	100.8	36.02	1.730	39.55	7.49	388.3	73.56	"
80.97	29.21	96.22	34.71	1.733	35.62	6.77	390.2	74.20	"
86.07	30.83	93.06	33.35	1.733	32.75	5.87	425.6	76.32	"
83.25	30.43	90.28	33.01	1.735	48.23	10.35	317.6	68.20	"
86.80	30.56	97.15	34.21	1.743	129.1	44.65	60.14	20.80	$Ca(ClO_3)_2 \cdot 2H_2O +$
84.41	30.69	90.78	32.99	1.742	136.2	50.47	33.57	12.44	$CaCl_2 \cdot 4H_2O$
84.11	30.70	89.60	32.81	1.748	139.5	50.83	35.08	12.78	"

86.23	31.49	87.63	32.01	1.725	139.5	50.86	34.72	10.79	$CaCl_2 \cdot 4H_2O$
82.11	31.51	78.47	30.11	1.718	115.0	43.79	47.63	18.15	"
86.47	34.69	62.80	25.20	1.659	144.8	53.56	25.52	9.44	"
84.20	35.59	52.40	22.14	1.641	132.4	52.40	20.29	8.03	"
88.76	36.91	51.76	21.52	1.625					
87.60	36.89	49.92	21.02	1.629	142.6	55.20	15.72	6.09	"
88.65	37.75	46.14	19.65	1.618	139.3	53.99	18.81	7.29	"
86.73	38.16	40.57	17.85	1.606	129.2	52.87	15.24	6.24	"
86.60	38.17	40.15	17.69	1.607					
83.90	37.92	37.42	16.91	1.614	142.6	57.59	5.02	2.02	"
86.95	38.82	37.09	16.55	1.603	131.3	52.87	17.00	6.85	"
86.93	40.15	26.62	12.29	1.578	137.7	56.67	5.29	2.18	"
87.80	40.53	29.03	13.41	1.580	132.1	53.91	12.85	5.25	"
90.32	41.70	26.28	12.12	1.565	133.9	55.05	9.41	3.87	"
85.73	41.22	22.25	10.70	1.570	134.2	56.25	4.33	1.81	"
88.28	42.82	17.94	8.70	1.562	125.3	55.19	1.83	0.81	$CaCl_2 \cdot 4H_2O$+
87.32	42.41	18.55	9.01	1.526	99.97	48.18	7.55	3.64	$CaCl_2 \cdot 6H_2O$
84.60	44.06	7.39	3.85	1.480	99.32	49.22	2.44	1.21	$CaCl_2 \cdot 6H_2O$
79.53	43.26	4.34	2.36	1.490	98.25	49.23	1.25	0.63	"
81.52	44.92	0.00	0.00	1.453					"

25 degrees C. without being transformed into the hexahydrate, for, if a line be drawn connecting the point marked $CaCl_2 \cdot 4H_2O$ with that marked water we find that this line does not cut the solubility curve of the tetrahydrate, hence it will be unstable when alone in the presence of water at this temperature[54]. It can however, as has been mentioned before, exist in contact with an aqueous solution containing a dehydrating salt such as in the present system.

The System $SrCl_2$–$Sr(NO_3)_2$–H_2O at 25 degrees C. Figure III and Table III.

The author's results for the solubility of $SrCl_2 \cdot 6H_2O$ are in excellent accord with the values given by Seidell [69] who states that the solubility at 25 degrees C. is 35.8% or 55.8

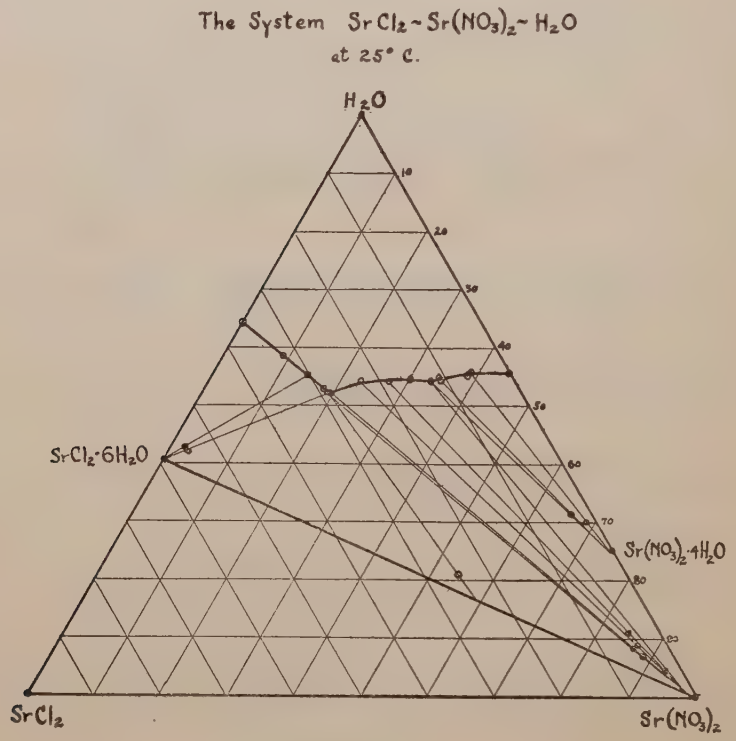

FIGURE III

TABLE III.

The System $SrCl_2 - Sr(NO_3)_2 - H_2O$
at 25 degrees C.

SOLUTION					REST				
$Sr(NO_3)_2$		$SrCl_2$			$Sr(NO_3)_2$		$SrCl_2$		
gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	Density 25 deg.	gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	Solid Phase
79.45	44.28	0.00	0.00	1.476					$Sr(NO_3)_2 \cdot 4H_2O$
70.33	38.69	11.49	6.32	1.492					
69.01	38.57	9.91	5.54	1.488	233.1	68.70	6.34	1.87	"
64.97	35.14	19.94	10.79	1.508					
62.51	34.29	19.82	10.87	1.510	210.0	65.71	9.50	2.97	"
62.23	33.71	22.35	12.11	1.513					$Sr(NO_3)_2$
62.17	33.72	22.20	12.04	1.513	2080.0	93.26	50.06	2.25	"
55.06	30.15	27.59	15.10	1.515					
50.53	27.25	34.95	18.83	1.523	1246.0	88.45	63.40	4.50	"
42.01	22.75	42.59	23.07	1.537	973.8	87.00	46.01	4.11	"
37.79	19.62	54.79	28.45	1.565	1024.0	86.43	59.90	5.06	"
36.33	18.91	55.72	29.01	1.571					
35.96	18.79	55.45	28.97	1.568	257.7	54.11	118.6	24.91	$Sr(NO_3)_2 +$ $SrCl_2 \cdot 6H_2O$
34.35	18.07	55.62	29.27	1.559					$SrCl_2 \cdot 6H_2O$
34.11	18.00	55.40	29.23	1.563					
25.56	14.10	55.75	30.75	1.526	7.12	2.99	131.3	55.09	"
15.51	9.07	55.64	32.51	1.483					"
0.00	0.00	55.80	35.82	1.403					"

grams $SrCl_2$ per 100 grams of water. According to Comey[63] the solubility is 56.9 grams per 100 grams of water at 25 degrees.

Comey[63] gives the solubility of $Sr(NO_3)_2$ as 79.0 grams per 100 grams of water at 25 degrees. Older results[70, 71] give by interpolation a value of 44.1% or 78.7 grams per 100 grams of water.

The solubility curve in this system is again one with three branches, a simple dehydration occurring as in the previous system. No double salt is formed. The left branch of the curve represents solutions in equilibrium with $SrCl_2 \cdot 6H_2O$. The central portion represents solutions in equilibrium with anhydrous $Sr(NO_3)_2$, and the right branch those in equilibrium with $Sr(NO_3)_2 \cdot 4H_2O$.

The System KNO_3–$Pb(NO_3)_2$–H_2O at 0 degrees C. Figure IV and Table IV.

The solubility of $Pb(NO_3)_2$ at 0 degrees is given by Glasstone and Saunders[30] as 28.70 weight per cent. Van Nostrand's manual[72] gives two sets of values, 26.74 and 27.95 weight per cent. Landolt, Börnstein and Roth[70] give 26.7 weight per cent. These values are in excellent agreement with those obtained by the author.

The solubility of KNO_3 at 0 degrees C. as given by Comey and Hahn[73] is 13.3 grams per 100 grams of water. Andreae[74] puts the solubility at 11.7 weight per cent.

The solubility curve in this system is composed of only two branches and no double salts are formed. Along the left branch will be found solutions in equilibrium with solid $Pb(NO_3)_2$ and along the right branch those in equilibrium with solid KNO_3.

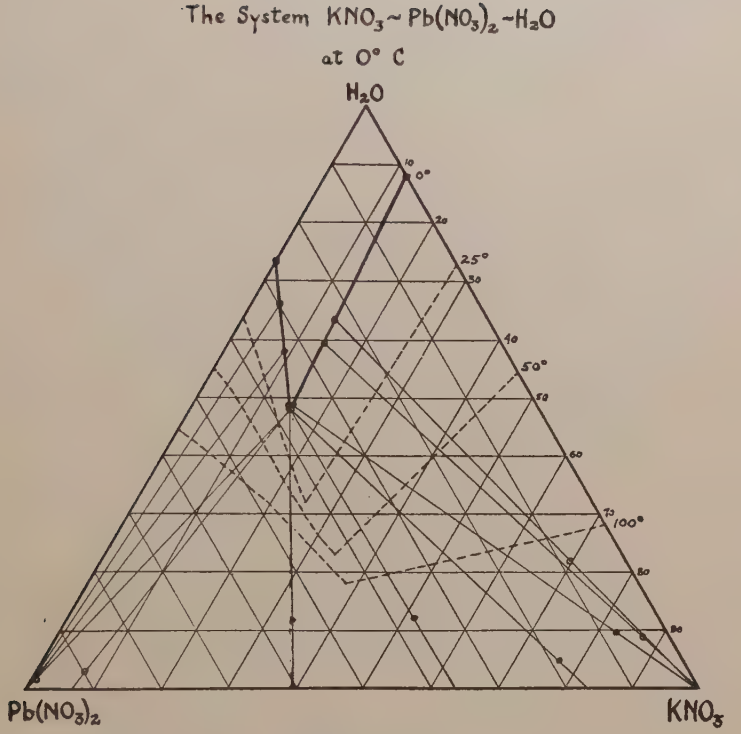
The System KNO_3 ~ $Pb(NO_3)_2$ ~ H_2O
at 0° C
H_2O
10
0°
20
25°
30
40
50°
50
60
75
100°
80
90
$Pb(NO_3)_2$
KNO_3

FIGURE IV

TABLE IV.

The System $KNO_3 - Pb(NO_3)_2 - H_2O$
at 0 degrees C.

SOLUTION				REST				
$Pb(NO_3)_2$		KNO_3		$Pb(NO_3)_2$		KNO_3		
gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	gms. per 100 g.H_2O	Wgt. %	Solid Phase
36.37	26.66	0.00	0.00					$Pb(NO_3)_2$
44.75	29.63	6.27	4.15	5751.0	97.56	43.97	0.75	"
56.66	32.94	15.40	8.95	6134.0	97.76	41.27	0.66	"
77.11	37.37	29.30	14.20	8561.0	98.70	14.03	0.16	"
77.07	37.12	30.56	14.74	2955.0	89.86	232.6	7.08	$Pb(NO_3)_2+KNO_3$
77.30	37.14	30.81	14.81	463.2	54.94	280.0	33.29	"
77.33	36.98	31.83	15.22	292.4	36.25	414.3	51.36	"
77.77	37.33	30.53	14.66	380.0	18.29	1597.0	76.87	"
74.25	36.27	30.49	14.89	78.45	7.55	861.1	82.87	KNO_3
43.23	26.05	22.71	14.33	43.36	3.92	962.5	87.06	"
36.21	22.95	21.57	13.67	40.91	8.82	322.5	69.60	"
0.00	0.00	13.95	12.24					"

DISCUSSION.

The fact that a stable double salt is formed between the two highly soluble electrolytes, $CaCl_2$ and $Ca(NO_3)_2$, shows conclusively that it is quite possible to have complexes formed in solutions of strong electrolytes even when the electrode potential diversity of the anions is very small, such as between Cl and NO_3 ions. The fact that $SrCl_2$ and $Sr(NO_3)_2$ do not form a complex compound at 25 degrees C. and also that $BaCl_2$ and $Ba(NO_3)_2$ [75, 70] show even a lesser tendency toward compound formation seems again to substantiate the general rule[1, 4, 29] that the tendency to form complexes increases as the electrode potential decreases. Thus, keeping the anions the same, we have an increasing tendency toward compound formation as we go from Ba to Sr to Ca ion. This same tendency is shown in the affinity of these ions for water, thus calcium salts are the most hydrated and the most soluble, strontium salts less so, and barium salts least. From the point of view of the Werner theory of complex salts[77] the Ca ion may be said to possess the stronger co-ordinating or secondary valences, in fact a double salt with the formula $CaCl_2 \cdot Ca(NO_3)_2 \cdot 4H_2O$ might be regarded as held together by those secondary valences on each Ca ion which have been vacated by water molecules.

It is interesting to note that the order of increasing tendency to form addition compounds among the alkaline earth chlorides is also that of increasing activity coefficients, thus both the observed activity coefficients as well as those calculated for a 1 molar solution by means of the Debye-Hückel equation[78], agree fairly well on the activity coefficients of $BaCl_2$, $SrCl_2$ and $CaCl_2$ as 0.397, 0.454, 0.673 respectively.

At first sight it may seem as though the formation of the above mentioned double salt is a contradiction of the general rule stating that addition compounds are more stable the more diverse the constituent groups. In accordance with this rule one would hardly expect an addition compound to be formed between $CaCl_2$ and $Ca(NO_3)_2$. However, as has already been mentioned in the introduction, it is just the marked similarity between the Cl and NO_3 group that would tend to make com-

bination possible. According to Kendall and Gross[79] little or no increase in molecular complexity, due to addition compound formation, is to be expected in a mixture composed of two components essentially similar in character, rather, there will be a dissociation (in this case ionization) of any complex molecules of the pure components, followed finally by a re-combination usually in the form of a substitution compound. It is only because of the marked similarity of two such components that one can substitute for the other. Kendall and his associates[7,80] in later papers, found this rule to be valid in quite a number of cases.

These considerations have led the author to believe that the complex formed in the system $CaCl_2$–$Ca(NO_3)_2$–H_2O is to be regarded, not as an addition, but rather as a substitution compound of the type: $CaClNO_3$, in which the closely similar Cl and NO_3 groups substitute for each other. Ordinarily when two compounds are closely similar in their constituent groups they possess the same crystalline form (Mitscherlich's Law). In such cases dissociation and re-combination of the various molecular and ionic species present in a mixture will evidently result in an almost "haphazard" replacement of the different radicals by one another at all points of the original molecules. The result is, solid solutions or mixed crystals are formed. In the present case the crystalline forms are different ($CaCl_2 \cdot 4H_2O$-rhombic; $Ca(NO_3)_2 \cdot 4H_2O$-monoclinic). The formation of the above substitution compound is very likely due to the fact that there exist certain attractive forces between the constituent groups, these forces being such that a certain substitution complex, in this case of the form $CaClNO_3$, predominates in stability. This being the case, it is not at all surprising that, given the proper conditions, a complex of this sort may be isolated. Whether the complex as isolated has the composition $CaCl_2$–$Ca(NO_3)_2$–$4H_2O$ or $CaClNO_3$–$2H_2O$ is difficult to tell. From the standpoint of solutions it is really a matter of small concern for according to modern theories of solution the salt is completely ionized. The composition in the solid state could only be definitely shown from X-ray crystal structure measurements.

Even though the anions in the system $CaCl_2$–$Ca(ClO_3)_2$–H_2O are similar as far as electronegativity is concerned, and a substitution compound might therefor be expected, we note the absence, at 25 degrees, of any such stable compound. This illustrates very well the fact that there is never any certainty about, or general rule for, the formation of stable, isolable substitution compounds in solution. Whether a substitution compound will be isolable or not depends entirely upon whether or not it is more or less soluble than the salts from which it is formed. If its solubility is less it will be isolable, if greater, the solution will first become saturated with respect to the simple salts and they will exist in stable equilibrium with solution. Since the rules governing solubilities of salts are as yet not sufficiently understood, we are not able to predict what the solubility of a complex compound will be and hence cannot predict its stability. It was for this reason that the author chose very soluble salts in the systems studied in the hope that the solubility of any complex that might be formed would be less than the solubilities of its constituent salts, thus insuring the stable existence of the complex in contact with solution. From the above it will be seen that the absence of a stable complex in the system $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25 degrees is thus not to be taken to preclude the existence of a complex. It may simply be that the complex has a solubility greater than its constituent salts at this temperature.

Another conclusion which may be drawn from the nonformation of a complex in the last mentioned system is that, in all likelihood, there will be no compounds formed in the systems:

$SrCl_2$–$Sr(ClO_3)_2$–H_2O at 25 degrees C.

$BaCl_2$–$Ba(ClO_3)_2$–H_2O at 25 degrees C.

This conclusion follows directly from the rule that compound formation decreases as electrode potential increases.

A glance at Figure IV shows that, contrary to expectations, no complex compound is formed in the solid state in the system KNO_3–$Pb(NO_3)_2$–H_2O at 0 degrees. When this isotherm is compared with those obtained by Glasstone and Saunders[30] at 25, 50, and 100 degrees (Fig. IV) it immediately becomes

apparent that both branches of the solubility curve become more steep as the temperature is lowered. It will be seen that at 0 degrees, as at the other temperatures, instead of the solubility of $Pb(NO_3)_2$ being diminished by the addition of KNO_3 it is very much increased. The same is true of the influence of $Pb(NO_3)_2$ on KNO_3 but to a lesser extent. It is quite evident that at least two opposing factors are in operation in this system, one, the usual competition of the salts or of the ions of the salts for the solvent[81], and second, complex ion formation[82]. The first of these factors tends to decrease the solubility of a salt when another salt is added. The second always tends to increase the solubility of a salt[83].

Since the increase in solubility, or "salting in," becomes more marked as the temperature is lowered it is quite evident that the complex ions formed by the two salts are more stable the lower the temperature. It is also evident that, although the complex can exist in solution at 0 degrees, it is not yet of the order of stability necessary for it to exist as a solid phase in equilibrium with a solution at that temperature.

Naturally, the author was led to suspect that, since the complex was becoming more and more stable, it might prove stable at a temperature lower than 0 degrees. However, experiments performed at –10 degrees C. with a mixture of $Pb(NO_3)_2$, KNO_3 and water calculated to yield the complex if it exists, showed no solid phase different from those already observed at 0 degrees. This would indicate that even at –10 degrees C. there is no isolable double salt of $Pb(NO_3)_2$ and KNO_3.

SUMMARY.

1. The solubility relations have been determined in the following ternary systems:

   I. $CaCl_2$–$Ca(NO_3)_2$–H_2O at 25 degrees C.
   II. $CaCl_2$–$Ca(ClO_3)_2$–H_2O at 25 degrees C.
   III. $SrCl_2$–$Sr(NO_3)_2$–H_2O at 25 degrees C.
   IV. KNO_3–$Pb(NO_3)_2$–H_2O at 0 degrees C.

2. A new method for the preparation of pure $Ca(ClO_3)_2 \cdot 2H_2O$ is described.

3. The general rule, that the tendency toward complex formation increases as the electrode potential (positive or negative) decreases, has been found to apply in the alkaline earth systems studied.

4. A method of purifying and dehydrating crystals of $CaCl_2$ and $Ca(NO_3)_2$ is described.

5. The existence of a new stable double salt whose empirical formula is $CaCl_2 \cdot Ca(NO_3)_2 \cdot 4H_2O$ has been established. Reasons have been adduced to show that this salt is probably a simple substitution compound formed by the displacement of one simple negative radical by another, rather than an addition compound involving an increase in molecular complexity.

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